The University of Chicago

AN EFFICIENT NEW METHOD OF PREPARING DIBORANE; NEW REACTIONS FOR PREPARING BROMODIBORANE AND THE STABLER PENTABORANE, B_5H_9

A PART OF THE DISSERTATION SUBMITTED TO THE GRADUATE FACULTY IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By
ANTON BEHME BURG

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AN EFFICIENT NEW METHOD OF PREPARING DIBORANE; NEW REACTIONS FOR PREPARING BROMODIBORANE AND THE STABLER PENTABORANE, B_5H_9

The hydrides of boron, a group of highly reactive, unstable substances which have been investigated in an unusually ingenious and careful way by Stock and his co-workers,[1] evidently deserve much further experimental study. Many of their chemical reactions are difficult to understand and their formulas, six of which have been established beyond any doubt, (B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$), seem not to be explained by any widely applicable theory of valence and molecular structure.[2]

The main obstacle to the advance of knowledge of these substances has been the great difficulty and expense of preparing them in quantities sufficiently large for thorough study. Stock's preparation method,[3] which consists in the reaction between an acid in aqueous solution and an alloy of boron, seems to be inherently inefficient because the presence of water excludes the possibility of obtaining the instantly hydrolyzable diborane. The yields at best are only 3% and the process must be operated so slowly that a month of tedious work is required for the production of a few grams of a mixture of several hydrides.

At the suggestion of Professor H. I. Schlesinger this field of chemistry has been rendered more accessible to experiment, by the development of a comparatively efficient new method of preparing diborane. This method, which depends upon a hitherto unknown reaction, has been developed to such an extent that it is now practicable to prepare 55% yields of diborane at the rate of five to ten grams of the pure substance per week. Although we have not yet studied the reaction in sufficient detail to have a complete understanding of its mechanism, nor to be certain that we have found the most favorable conditions, we believe that the new method solves the problem of obtaining diborane in quantities suitable for long series of experimental work. We are therefore reporting the partially refined method at this time, along with some new reactions of diborane.

[1] Stock and others, *Ber.*, **63B**, 2927 (1930), and earlier papers there cited.

[2] Since the writing of this dissertation, Pauling, *J. Am. Chem. Soc.*, **53**, 3227 (1931), has developed a theoretical basis favoring Sidgwick's suggestion of single electron bonds between boron and hydrogen atoms in these compounds.

[3] Stock, Wiberg and Martini, *Z. anorg. Chem.*, **188**, 32 (1930), and earlier papers. Steele and Mills also have contributed improvements: *J. Chem. Soc.*, 74–79 (1930).

The method consists essentially of the reduction of gaseous boron trichloride by hydrogen in an electric discharge at low pressure. Boron and various non-volatile solid hydrides[4] are formed in the discharge chamber. The volatile reaction products are hydrogen chloride, small quantities of diborane, and large yields of an unstable substance which, by all available evidence, must be monochlorodiborane, B_2H_5Cl.[5] Under the most favorable conditions yet found about three-quarters of the boron chloride passes through the discharge without apparent change. The chlorodiborane apparently cannot be separated from this residual boron chloride by any physical means now available. The hydrogen chloride and the small quantity of diborane are separated by distillation from the boron chloride and chlorodiborane. When the residue is allowed to warm up to 0° most of the latter decomposes, evidently according to the equation $6B_2H_5Cl = 5B_2H_6 + 2BCl_3$.[6] The diborane is distilled off, and is easily purified by fractional condensation. If the residual mixture is allowed to stand further at 0°, more decomposition occurs. The process of decomposing the chlorodiborane and removing the resulting diborane may be continued until there remains only a trace of the former, very difficult to decompose in the presence of much boron chloride.

The fact that the decomposition stopped in mid-course unless the diborane was removed suggested that a measurable equilibrium occurred. To test this possibility we allowed gaseous diborane to remain in contact with liquid boron chloride. Under the conditions of the experiment about one-eighth of the diborane was absorbed to form the chloro derivative. The decomposition of the chlorodiborane was thus shown to be reversible to a practical extent. A similar experiment with boron bromide and diborane showed that the equilibrium $5B_2H_6 + 2BBr_3 = 6B_2H_5Br$ is even more favorable to the formation of the halogen derivative; by repeating six times a process of isolating the bromodiborane and remixing the residual reactants, we were able to convert practically all of a sample of boron bromide into bromodiborane. This reaction was found to be a convenient and efficient means of preparing bromodiborane. These reactions may also be of more general interest, in that they suggest the possibility of using diborane as a means of substituting hydrogen for halogens in the volatile

[4] Some of these are soluble in organic solvents but not in water; other components of the mixture are not soluble in any organic solvent tried but react readily with water or alkali solutions and explosively with concentrated nitric acid. We expect to investigate them more thoroughly after we have accumulated larger samples.

[5] The substance is spontaneously inflammable in air and is slightly more volatile than boron trichloride, whose boiling point is 12.5°. It is so unstable and so difficult to separate from boron chloride that we have not been able to perform a satisfactory analysis. Evidence which we shall present in the experimental part will show that it is extremely difficult to escape the conclusion that it is monochlorodiborane.

[6] Stock has observed such a reaction, *Ber.*, **47**, 3121 (1914).

halogen compounds of various other elements and also the possibility of easily halogenating the higher hydrides of boron by the use of the boron halides.

The small quantities of diborane directly produced by the reaction in the discharge always are mixed with large quantities of hydrogen chloride, whose complete removal is rather difficult. We have found that samples of diborane, from which most of the hydrogen chloride has been removed, may be completely purified by allowing them to stand for several months at room temperature. The hydrogen chloride is used up, evidently by the reaction $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$. The reaction proceeds without any catalyst other than glass or mercury.

On the other hand, when diborane containing a small quantity of hydrogen chloride is heated at 120–130°, in the absence of mercury, another reaction also takes place—a considerable portion of the diborane is converted into the stabler of the pentaboron hydrides, B_5H_9. The yields are sufficient to indicate that it is possible to prepare useful quantities of this substance from the now readily available diborane.

As a preliminary test, before an unsuccessful attempt to ethylate chlorodiborane, we treated diborane with excess zinc ethyl. The two reacted equimolarly, giving a white, partially sublimable solid whose further study has not been attempted.

Experimental Part

Preliminary Experiments.—The apparatus used for a preliminary experiment was similar to that used by Weintraub for the preparation of pure boron.[7] Pure hydrogen was bubbled through pure boron chloride at −40°, and the resulting gaseous mixture was passed through a glass-inclosed arc between water-cooled copper electrodes fed by a 250-volt ampere transformer giving a maximum potential of 15,000 volts. Boron was formed in the manner described by Weintraub and the inner walls of the inclosing bulb were coated with a light-brown partially water-soluble solid, evidently a mixture of non-volatile hydrides of boron. The volatile reaction products were condensed in a U-tube immersed in liquid air. The hydrogen chloride was boiled off at atmospheric pressure, and the residual boron chloride was found to contain a spontaneously inflammable substance, which formed a boron mirror on contact with hot glass.

The volatile products were studied further by the use of a vacuum apparatus designed according to the technical principles described by Stock.[8] The preliminary experiment was repeated, and most of the hydrogen chloride was removed in nearly pure

[7] Weintraub, *Trans. Am. Electrochem. Soc.*, **16**, 176–177 (1909).

[8] Stock, *Ber.*, **54A**, 142 (1921). Our apparatus was first built in very simple form and was amplified as the necessity for more parts arose. Although its present form is greatly different from the general design described by Stock, the principles of operation are not sufficiently different to justify a complete description in this place. It is made entirely of Pyrex glass except that the floats in the mercury valves are of ordinary soft soda-lime glass.

condition by the method of fractional condensation. All attempts to separate the small quantity of spontaneously inflammable substance from boron chloride failed completely. During these attempts the vapor pressures of various fractions were measured at 0°. In all cases the values were higher than that of pure boron chloride (477 mm.), and they always increased slowly during measurement. The rise of the vapor pressure was found to be a result of the formation of small quantities of a gas somewhat more volatile than hydrogen chloride (a typical vapor pressure at −112° was 248 mm.), by decomposition of the spontaneously inflammable substance. A sample of this gas was purified as much as possible with the facilities then available, but it still contained some hydrogen chloride. The volume and weight of the sample were determined, and an indirect analysis was performed by passing the gas through a hot quartz tube and determining the resulting hydrogen, boron, and boron chloride, and the residual hydrogen chloride. The formula calculated from the results was $B_2H_{5.7}$. Although the analysis was very rough, it showed beyond reasonable doubt that the highly volatile decomposition product was diborane (B_2H_6) and suggested that the substance from which it formed was a chloro derivative.[9]

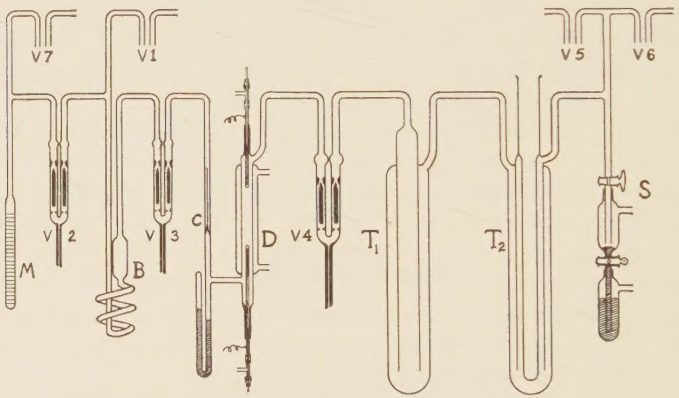

Fig. 1.

It was evident that any considerable improvement of the yield would require that the production of boron be diminished. Experiments in which the hydrogen passed alone through the arc and met the boron chloride just after leaving that source of activation led to no useful result—it seemed that the boron chloride must react with the hydrogen in the arc or not at all. Experiments in which the gas mixtures were led through a fine capillary tube into a discharge 75–100 cm. long, at pressures in the neighborhood of 1 mm., gave better yields than those from the preliminary experiments at atmospheric pressure. But the process was slow, and the formation of comparatively large quantities of the non-volatile solid hydrides indicated a very serious loss of the volatile hydrides.

Most Favorable Conditions for the Reaction.—To avoid these disadvantages we planned a series of experiments at higher pressures, to be run with higher flow rates and with the electrodes set at shorter distances apart. For these experiments we set up the apparatus represented in the diagram. It is connected to the main apparatus by way of valves 5 and 7. Samples of boron chloride are measured in the graduated tube M, and are then distilled into the spiral bubbler tube B. Hydrogen, drawn from

[9] More satisfactory analyses and other evidence presented later in this paper confirm these conclusions.

a cylinder and freed from oxygen by passage successively through a tube filled with platinized silica gel at 500° and a liquid air trap, enters through valve 1 and passes at atmospheric pressure through the bubbler. The concentration of boron chloride in the resulting gaseous mixture is controlled by adjusting the temperature of a liquid ammonia bath in which the bubbler is immersed. The mixture streams through the capillary tube C, which determines the rate of flow, into the discharge chamber D. The pressure in the apparatus beyond the capillary tube is held at a few millimeters by a pump connected through the stopcock S. The water-cooled discharge chamber D, which has a length of 20 cm., internal diameter 13 mm. and wall thickness 1 mm., is sealed to end-tubes just wide enough to receive the 6-mm. water-cooled copper electrodes. The vacuum-tight connections from copper to glass are made by the use of picein wax, which allows the adjustment of the distance of separation of the electrodes before each experiment.

After reacting in the discharge, the gaseous mixture enters the condensing tube T_1, which is immersed in liquid air. Nearly all of the condensable part of the mixture is trapped in that place, yet small quantities of diborane and hydrogen chloride pass through with the hydrogen if the stream is very rapid. These last traces are trapped in the somewhat colder condensing tube T_2. This trap is immersed in liquid air, and its innermost tube contains liquid air under 20–30 mm. pressure (temperature about −210°). The hydrogen which passes this tube never contains the least detectable trace of diborane or hydrogen chloride.

At the end of the operation valve 4 is closed and mercury is allowed to rise into the tube above stopcock S. The hydrogen is then completely pumped out through valve 6, and the condensates are distilled through valve 5 into the main vacuum apparatus for separation by distillation methods.

In each experiment the volume of hydrogen chloride produced was taken as the measure of the reduction of the boron chloride. For purposes of comparison between the experiments this quantity was divided by three, to convert it to the equivalent volume of boron chloride, and expressed as the percentage of the boron chloride used up by the reaction. As much of the diborane as could be obtained in pure condition (as evidenced by its 224 mm. vapor pressure at −112°) was measured as such; the rest, either contaminated with hydrogen chloride or existing in the latent form of the chloro derivative, was determined by the quantity of hydrogen produced by hydrolysis (each B—H bond produces one molecule of hydrogen). The yields were calculated by comparing the quantity of boron in the hydride form with the quantity of boron in the boron chloride destroyed by the reaction. Boron chloride which could have been regained by the complete decomposition of the chloro derivative was counted as not destroyed.

The conditions and results of the eight most significant experiments are listed in the table. In this table the flow rate is expressed as the volume

EXPERIMENTAL RESULTS

Total pressure in the discharge, mm.	Flow rate, cc./min.	Ratio H_2/BCl_3	Length of discharge, cm.	Time, hrs.	Boron chloride used up, %	Yield of diborane, %
5.0	30	8.0	11	3.5	77	7
4.0	30	9.0	20	4.0	70	6
7.6	30	7.5	7	3.0	44	10
7.5	105	10.5	7	1.7	38	32
6.0	95	20.0	7	5.5	62	14
20.0	300	10.0	7	1.7	26	60
12–30	300	10.5	7	15.0	25	30
9.0	300	12.0	7	16.5	26	60

of pure hydrogen at atmospheric pressure which will flow through the capillary tube under one atmosphere difference of pressure. In all experiments the full power of the 15,000 volt, 250 VA transformer was used for maintaining the discharge.

The yield of diborane directly produced varied from 3 to 5%. The rest appeared as the chloro derivative.

It is apparent from this table that all changes which decrease the time spent in traversing the discharge tend to improve the yield. The first three experiments show that decreasing the length of the discharge improved the results. Comparison of the fourth and fifth shows that low concentrations of boron chloride are to be avoided. It appears from the results of the last three experiments that the pressure should not be allowed to rise above 20 mm. Comparison of these three groups of experiments shows beyond any doubt that high rates of flow are advantageous.

It is probable that there occurs in the discharge a complex set of equilibria between activated hydrogen, boron chloride, diborane and its chloro derivatives, and hydrogen chloride; without such an assumption it is very difficult to account for the production of such large quantities of a substance as unstable as chlorodiborane. There are also side reactions, probably due to the heat of the discharge, which produce the boron and the non-volatile hydrides. For the very best possible results, therefore, we must establish equilibrium conditions as favorable as possible to the formation of hydrides, and then remove the products as rapidly as possible from the region of action.

Preparation of Diborane.—As an example of the preparation of diborane by the decomposition of the chloro derivative we now present the details of the last of the experiments listed in the table. In this experiment 17.8 liters[10] of tensiometrically uniform boron chloride was added to the hydrogen stream at −43°, and passed through the discharge at 9 mm. total pressure. There was formed 14.06 liters of hydrogen chloride, corresponding to the destruction of 4.69 liters of boron chloride. About 150 cc. of diborane was directly produced and was isolated in 90% purity by repeated fractional condensation through a U-tube at −140°. The mixture of boron chloride and chlorodiborane was freed from hydrogen chloride and then allowed to warm up to 0°. After four hours 700 cc. of nearly pure diborane was distilled off. The residue was allowed to stand at 0° and a further 200 cc. of diborane was produced. The process was continued and smaller and smaller quantities of diborane were formed. The time of standing seemed to have little effect on the amount of decomposition during each period of standing; a condition of equilibrium was suggested, according to the equation

[10] Unless otherwise specified, all volumes recorded in this paper refer to the gaseous state at 0° and 760 mm. pressure.

$6B_2H_5Cl = 5B_2H_6 + 2BCl_3$. It seemed impracticable to continue the decomposition process after the vapor pressure of the residue at 0° had fallen to 500 mm. The samples of diborane were completely purified by distilling them through a U-tube at −140°. The experiment yielded 1150 cc. of pure diborane (its vapor pressure at −112° was 224 mm.). The whole 1300 cc. of diborane corresponded to 2.60 liters of boron chloride, or 55.5% of the boron chloride destroyed. A further 4–5% yield remained in the residual boron chloride as chlorodiborane.

Samples of diborane contaminated with hydrogen chloride are very difficult to purify by distillation methods. In order to learn whether the hydrogen chloride could profitably be eliminated by the reaction $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$,[11] we placed in a sealed 200-cc. bulb about 65 cc. of a mixture of diborane and hydrogen chloride containing about 30% of the latter. After three months at room temperature the sample was freed from the resulting hydrogen and separated by fractional condensation into three components—0.57 cc. of the unstable pentaborane B_5H_{11}, 12 cc. of an inseparable mixture of boron chloride, chlorodiborane, and probably tetraborane (recognized by its slow hydrolysis), and 33.5 cc. of diborane nearly free from hydrogen chloride (its vapor pressure at −112° was 228 mm., instead of 224). Hydrolytic analyses of two portions of the diborane sample gave the empirical formulas $B_{1.97}H_6$ and $B_{2.03}H_6$. There was not enough hydrochloric acid present in the boric acid solutions to change the neutral color of methyl orange. These analyses showed that the reaction of diborane with hydrogen chloride goes practically to completion without the use of any special catalyst, other than glass or mercury, and they also removed the last possible doubt that we have been dealing with diborane.

In order to determine whether a condition of equilibrium was the reason for the difficulty of decomposing the last of the chlorodiborane in the presence of much boron chloride, we carried out an experiment in which 144 cc. of pure boron chloride and 121 cc. of pure diborane were mixed and allowed to stand. At the start the mixture was separated into its constituents—it was found that a quantitative separation could be accomplished by distilling through a U-tube at −130°. The constituents were remixed and allowed to stand for two and one-half hours at room temperature in a 600-cc. bulb containing finely divided mercury. The quantitative separation was again easily accomplished—no reaction had occurred. The substances were again remixed and allowed to stand for eight hours with most of the boron chloride in the liquid state at 0° (total pressure near atmospheric). Then the separation was again attempted. It was at once obvious that a reaction had occurred: only 105 cc. of the original 121 cc. of diborane could be regained by fractional condensation and the condensate at −130° was partially liquid (pure boron chloride would have been entirely solid). This condensate contained a considerable quantity of a spontaneously inflammable gas and its vapor pressure at 0° was at first 580 mm., but rose to 685 mm. in the course of five minutes. Such behavior is typical of mixtures of chlorodiborane and boron chloride. The experiment eliminated all doubt that the decomposition of chlorodiborane is reversible.

[11] Analogous reactions have been observed by Stock and Kusz, *Ber.*, **56B**, 800 (1923); Stock and Pohland, *ibid.*, **59B**, 2223 (1926).

Preparation of Bromo Diborane.—A similar reaction between diborane and boron tribromide also was observed. A sample of boron bromide was fractionally distilled until it was tensiometrically uniform at 20° (vapor pressure 54 mm.) and a portion of it, measured as a liquid and calculated as 150 cc. of gas, was condensed in a U-tube provided with a long U-manometer. It was then treated with 260 cc. of pure diborane which was kept at a pressure somewhat higher than atmospheric by allowing it to evaporate from an adjacent U-tube at −78°. After the last of the diborane had evaporated, as a result of absorption by the boron bromide, the reaction tube was alternately cooled with liquid air and warmed to room temperature, in order to insure good mixing of the reactants. When the vapor pressure of the mixture, measured at 0° and with 80 cc. as the volume of the apparatus, had reached an apparently constant value of 960 mm., it was supposed that the reaction had reached equilibrium. The mixture was then separated by fractional condensation (U-tube I at −78°; II at −135°; III at −190°)[12] and only 95 cc. of the original 260 cc. of diborane was regained. This residual diborane was remixed with the I condensate and a further 297 cc. of pure diborane was added. The mixture was brought to equilibrium as before and the fractional condensation was repeated. The I and III condensates were then remixed. This process was repeated six times, after which there remained only 12 cc. of gas completely condensable at −78°; the fact that the volume of this fraction quickly increased to 14 cc. on standing at room temperature makes it reasonable to suppose that it was largely dibromodiborane, a very unstable substance whose decomposition increases the volume. There remained 220 cc. of excess diborane. The quantity of diborane absorbed (337 cc.) and the quantity of boron bromide used up (about 140 cc.) agreed reasonably well with the equation $2BBr_3 + 5B_2H_6 = 6B_2H_5Br$.

The combined II condensates were subjected to further fractional condensations between narrower limits of temperature until the main sample was practically uniform. Its vapor pressure at −44° was 42 mm.; this value agrees with that predicted from the vapor pressures given by Stock, Kusz and Priesz[13] for pure bromodiborane. An analysis, made by hydrolyzing a 60-cc. sample of the material in a sealed bulb, measuring the resulting hydrogen, and titrating successively the hydrobromic and boric acids, gave the empirical formula $B_{2.02}H_{4.96}Br_{1.05}$, in good agreement with the formula B_2H_5Br. We believe that this new method of preparing bromodiborane presents considerable advantage over that used by Stock, Kusz and Priesz in that it can be made to give practically quantitative

[12] In describing the results of a fractional condensation we designate the successive U-tubes through which the mixture is distilled as I, II, III, etc., and refer to the condensates which appear in these tubes as the I condensate, the II condensate, etc., respectively.

[13] Stock, Kusz and Priesz, *Ber.*, **47**, 3139 (1914).

yields, and does not require special apparatus for handling bromine under vacuum conditions. The time required for the preparation as here described was only two days (not including the time required for preparing the pure reactants).

The remaining sample of bromodiborane (344 cc.) was used for an investigation of the ease of decomposition. The sample was allowed to remain for forty-five minutes at room temperature in an apparatus volume of 140 cc. The decomposition products were separated from the residual bromodiborane, and it was found that 55% of the sample had decomposed. The residual bromodiborane was allowed to stand further under the same conditions. By six repetitions of the process of decomposing bromodiborane and isolating the products it was found possible to regain 98% of the diborane used to form the sample. It seems to be about as easy to obtain quantitative decomposition of bromodiborane as quantitative preparation.

Attempts to Identify Chloro Diborane.—The products of most of the experiments listed in the table, and of several others not listed, were employed for attempts to isolate the chloro derivative for positive identification by analysis. Many different conditions of distillation, none of them effective for the purpose, were tried. The extreme tendency of the substance to decompose, giving as one of the products the substance from which it is so difficult to separate, boron chloride, made the problem extraordinarily difficult. It is probable that it forms constant boiling mixtures with boron chloride, mixtures which cannot be resolved by distillation at different pressures because the decomposition is very rapid at pressures higher than a few millimeters. The most nearly successful attempt at separation was carried out by the use of a fractionating column connected to the vacuum system.

In this instrument, the mixture being fractionated is refluxed through a silvered and evacuated double-walled column by means of an aluminum block kept at a suitably low temperature by the use of liquid air or solid carbon dioxide. The vapors escaping reflux pass through a mercury bubbler, by which the fraction refluxed may be controlled, into the main part of the vacuum apparatus. This column, used for purifying a 250-g. sample of boron chloride (reflux temperature $-78°$), delivered a sample so pure that every fraction, even down to the last 30 cc. of gas, showed the same vapor pressure at $0°$ (477 mm.). It was also used for removing every trace of hydrogen chloride from some of the larger samples of discharge reaction products.

The products of the seventh of the experiments listed in the table were freed from hydrogen chloride by the use of the fractionating column (reflux temperature about $-107°$, rising a few degrees near the end of the process) and then the distillation was continued with the refluxing block at $-75°$. Occasional samples of the distillate were taken out and roughly analyzed by hydrolysis. The first samples gave about two volumes of hydrogen and those taken just before the distillation was stopped gave about one-eighth as much. The whole distillate, about 6 cc. of liquid, was subjected to a fractional condensation starting in a continuously agitated tube whose temperature rose slowly from -124 to $-78°$: the distillate traversed the

U-tubes I at $-112°$, II at $-124°$, III at $-135°$ and IV at $-190°$. The IV condensate consisted of nearly pure diborane. The quantity, 175 cc., indicated that nearly half of the desired substance had decomposed during the process of fractionation. The II condensate contained boron chloride and a concentration of hydride equivalent to 10% diborane. The I condensate contained less hydride but still was far from being pure boron chloride. The III condensate consisted of about 1 cc. of liquid which showed a vapor pressure of 2 mm. at $-112°$. This sample was subjected to further fractional condensation under the same conditions but no further separation occurred; the IV condensate was negligible and both the II and III condensates gave slightly more than two volumes of hydrogen when small portions were hydrolyzed. This result makes it reasonable to believe that a constant boiling mixture was obtained. The possibility that the substance in question might be chloromonoborane, BH_2Cl, was negated by the observation that the gaseous volume of a concentrated sample increases during the decomposition. Attempts at indirect analysis of portions of the III condensate led to unsatisfactory results because it was impossible to measure accurately the volume of a sample undergoing such rapid decomposition. In two cases, however, the volume of the partially decomposed sample was measured and then the diborane was removed by distillation from a tube at $-125°$. The volume of the residue was then indirectly determined by measuring the volume of the diborane. Hydrolytic analyses of these residues gave values of the hydrogen, boron and chlorine indicating formulas between B_2H_5Cl and B_2H_6. But these results were somewhat untrustworthy because the low concentration of hydride in these residues (about 8%, expressed as diborane) made the determination too sensitive to experimental errors.

We may now summarize the evidence bearing on the constitution of the spontaneously inflammable product of the reaction in the discharge. We have the following reasons for believing that it is monochlorodiborane.

1. The rapid decomposition of even concentrated samples of the substance in the presence of boron chloride at room temperature or lower never produces detectable quantities of any substance other than diborane and boron chloride. The decomposition of the substance causes an increase in the gaseous volume. The only conceivable type of substance fitting both of these facts would be a chloro derivative of diborane.

2. From the difference in the boiling points of bromoethane (38°) and monobromodiborane (10°) and the boiling point of chloroethane (12.5°) we should predict that the boiling point of monochlorodiborane would lie between -10 and $-20°$. By a similar analogy we should predict that the boiling point of dichlorodiborane would be at least 30°. The substance in question is definitely more volatile than boron chloride, whose boiling point is 12.5°; it therefore must be monochlorodiborane.

3. From the work of Stock, Kusz and Priesz[14] it appears that polyhalogen derivatives of diborane are far less stable than the corresponding monohalogen derivatives. The chance that we obtained dichlorodiborane and no monochlorodiborane therefore seems vanishingly small.

4. Treatment of diborane with boron bromide gives almost exclusively monobromodiborane. Treatment of diborane with boron chloride under similar conditions gives the substance whose identity we seek to establish.

5. Rough indirect analyses gave results favoring the formula B_2H_5Cl and not even hinting at $B_2H_4Cl_2$.

From this mass of evidence we must conclude that the spontaneously inflammable product of the reduction of boron chloride in the electric discharge is monochlorodiborane.

In the course of experiments for the establishment of the identity of this substance it was thought that the replacement of the chlorine by reaction with zinc ethyl might offer a means of determining definitely which chloro derivative of diborane was present. In order to determine first whether zinc ethyl would attack any part of the molecule other than the boron–chlorine bond, we performed an experiment in which 9 cc. of diborane was allowed to stand for nine hours in contact with 0.25 cc. (liquid at 0°) of zinc ethyl. The diborane was slowly but completely absorbed to form a white solid. About 0.04 cc. (liquid) of the zinc ethyl, corresponding to about 10 cc. gas, was used up by the reaction. Heating of the white solid for fifteen minutes at 90° caused it to turn gray and evolve a white sublimate and 5.6 cc. of hydrogen. The dark residue was found to react with water to produce very small quantities of an inflammable gas. Treating a mixture of boron chloride and chlorodiborane with zinc ethyl gave a similar white solid, mixed with zinc chloride.

Preparation of Pentaboron Hydride.—We have mentioned that diborane reacts with hydrogen chloride slowly at room temperature to give chlorodiborane and boron chloride and at the same time produces the usual decomposition products of pure diborane. We have also found that heating a mixture of diborane and hydrogen chloride in the absence of mercury causes a reaction by which the stabler of the pentaboron hydrides, B_5H_9, is produced. A mixture containing about 105 cc. of diborane and 15 cc. of hydrogen chloride was distilled through a U-tube at −78°, to exclude mercury vapor, and condensed in a narrow tube connected to a 500-cc. bulb and to a drawn-down tube of a size to fit the vacuum tube opener. The bulb with its appurtenances was sealed off from the main vacuum apparatus and immersed for forty-eight hours in an oil-bath maintained at 120–130°. The inner walls of the bulb became coated with a light brown solid and small quantities of decaborane ($B_{10}H_{14}$) and a less volatile yellow solid condensed in the cool tube above. The

[14] Stock, Kusz and Priesz, *Ber.*, **47**, 3115–3149 (1914).

system was then opened and 180 cc. of hydrogen was pumped out. The products condensable by liquid air were separated by fractional condensation. The mixture contained 12 cc. of diborane, 6 cc. of an inseparable mixture of chlorodiborane and boron chloride, and 9 cc. of a substance which showed a uniform vapor pressure of 65 mm. at 0° and whose melting point was roughly measured as −45°. This substance was so stable that it did not change in any way on standing for a week in the gaseous state at room temperature. Although an accident prevented an elementary analysis, there can be no doubt that it was B_5H_9, a comparatively stable substance which, according to measurements by Stock and Kusz,[15] has a vapor pressure of 65 mm. at 0° and a melting point of −46.9°. According to the equation $5B_2H_6 \longrightarrow 2B_5H_9 + 6H_2$ the yield of B_5H_9 was about 20%. This is an entirely new reaction; the direct production of this substance from diborane has never before been reported. This reaction promises to be the means of making B_5H_9 readily available for experiment.

Summary

Sixty per cent. yields of chlorodiborane were obtained by the reduction of boron trichloride by hydrogen in a high-tension electric discharge at low pressure and under carefully adjusted conditions. Although the product cannot be separated from the residual boron chloride, it can readily be decomposed to produce diborane, which may thus easily be prepared in quantities suitable for experimental work on a comparatively large scale. This decomposition was shown to be reversible; the reaction of boron chloride with diborane produces some chlorodiborane. It also was found that boron tribromide and diborane react to form relatively large quantities of bromodiborane, and that the reaction may be used as a convenient quantitative method for the preparation of this substance.

Diborane was found to react slowly with hydrogen chloride at room temperature to produce chlorodiborane and boron chloride. At a higher temperature the reaction is much more rapid, and at the same time there occurs a hitherto unknown reaction by which as much as 20% of the diborane is converted into the stable pentaboron hydride B_5H_9.

Zinc ethyl reacts with diborane to produce a white solid whose constitution has not yet been determined.

The author wishes to express his deep appreciation of the confidence and able guidance of Professor H. I. Schlesinger.

[15] Stock and Kusz, *Ber.*, **56B,** 801 (1923).